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EVIDENCE OF THE INTERCALATIVE REDOX POLYMERIZATION OF ETHYLENEDIOXYTHIOPHENE INTO V_2O_5; ACHIEVEMENT OF HIGHLY CONDUCTING POLY(3,4-ETHYLENEDIOXYTHIOPHENE)/V_2O_5 NANOHYBRIDS

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We have established a novel method of inserting poly(3,4-ethylenedioxythiophene) (PEDOT) between the layers of V_2O_5 using a soft process of intercalation. The reaction takes place with the *in situ* polymerization of EDOT within the framework of crystalline V_2O_5 with different nominal EDOT/V_2O_5 ratios. The hybrids PEDOT/V_2O_5 exhibit a high electrical conductivity.

Keywords: Intercalative redox polymerization; Nano-hybrids; High conductivity

1 INTRODUCTION

Recent progress in 'nano-chemistry' gives birth to a new emerging area, so-called 'hybrid' or 'nanocomposite', which is a challenge for combining properties of two or more different species into a unique material [1–4]. For instance, conducting polymer/V_2O_5 hybrids have received significant attention over the past several years to profitably integrate desirable properties of the vanadium oxide and of the polymeric counterpart [5–12]. Especially, in the field of lithium battery, V_2O_5 is one of the most beneficial lithium cathodes with processability and high capacity, whereas conducting polymers have advantages including flexibility and conductivity. From an academic point of view, there remain interesting things to be investigated such as the nature of interactions between the p-type polymer (most conducting polymers have a p-type character) and the n-type vanadium oxide, and also the influence of

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these interactions on the overall electrical properties. These hybrids are generally prepared by mixing V_2O_5 gel with monomers of the corresponding conducting polymer such as polyaniline (PANI), polypyrrole (PPY), or polythiophene (PTH) [5–15]. For some selected conducting polymers, their chemical structure is shown in Figure 1. The PANI/V_2O_5 xerogel system is the most intensively studied [5, 6, 10–15]. The reaction between aniline and V_2O_5 xerogel proceeds via oxidative intercalation and subsequent polymerization of the aniline monomer concomitant with the reduction of V(V) to V(IV) in the xerogel host. Kanatzidis *et al.* found that the growth of polymer goes on mainly within the interlamellar space with the consumption of oxygen [15]. Aging in air causes both partial reoxidation of the inorganic host, that is auto-recovery of V(V) from V(IV), and the post-polymerization of the organic intercalate. Lira-Cantú *et al.* optimized the oxygen treatment condition and reported that the thermal treatment under oxygen over 80 °C for more than 5 hr may destroy the polymer chain [10–12]. On the contrary, hybrid systems based on PPY/V_2O_5 or PTH/V_2O_5 are relatively less studied. The position of the heteroatom makes a distinction in the chemistry and physical–chemical properties between PANI on one side and PPY or PTH on the other side [16]. The N atom of PANI is outside the ring and participates directly in the polymerization process, whereas the heteroatom N or S for PPY or PTH, respectively, is one of the ring component members and, instead, the alpha carbon takes part in the polymer linkage. Concerning PPY/V_2O_5 hybrids, it was reported that only a partial reoxidation was attained even after 72 hr O_2 exposure at 150 °C. On the other hand, the hybrids prepared under reflux conditions have fully oxidized vanadium [6, 7]. As for the PTH/V_2O_5 hybrids, the thiophene monomer is not easy to insert directly into V_2O_5, because thiophene is reported to have a slightly greater redox potential ($\sim$3.8 V *vs.* Li^+/Li) than V_2O_5 ($\sim$3.4 V *vs.* Li^+/Li). However, Goward *et al.* successfully achieved the synthesis of several PTH/V_2O_5 hybrids with bithiophene, *ter*thiophene, 3-methyl thiophene, and 2,5-methyl thiophene, [7]. Regarding 3-methyl thiophene, the methylation in the position 3 facilitates α–α' coupling and thereupon a more regular structure, whereas in the case of 2,5-dimethyl thiophene, α–β' or/and β–β' coupling deteriorates polymer order.
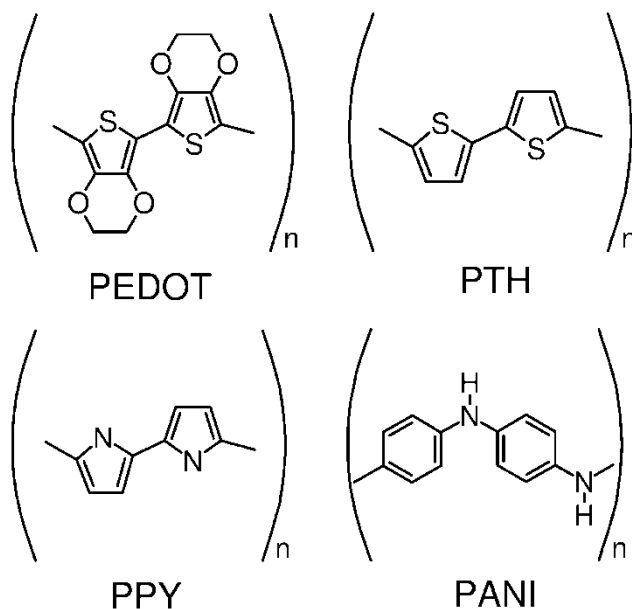

FIGURE 1   Chemical structure of some selected conductive polymers: PEDOT, PTH, PPY and PANI.

2 CHOICE OF POLY(3,4-ETHYLENEDIOXYTHIOPHENE) AS INTERCALATE INTO V$_2$O$_5$

The conductivity of the hybrids (such as those quoted above) seems to be sensitive to both polymer nature and overall polymer order in the material [5, 15]. That is, a more regular order leads to higher conductivity [16]. In this standpoint, PEDOT is expected to form with V$_2$O$_5$ a hybrid system with high conductivity because its cap in positions 3 and 4 with the ethylenedioxy group would lead to the most regular polymeric order. The PEDOT has indeed been reported to exhibit the best electrical conductivity among known polymers, up to $550\,\mathrm{S\,cm^{-1}}$. Moreover, its air-stability is superior to that of PANI, PPY, and PTH [17, 18].

In the following, we will describe a systematic study of PEDOT/V$_2$O$_5$ hybrids, which gives evidence of the intercalation of PEDOT within the interlamellar space of well-crystalline V$_2$O$_5$, leading to an overall high electrical conductivity.

3 SAMPLE PREPARATION AND CHEMICAL COMPOSITION

Although we have previously described the sample preparation in detail [19–21], let us simply recall here that the PEDOT/V$_2$O$_5$ hybrids were synthesized by insertion and subsequent polymerization of EDOT into well-crystalline V$_2$O$_5$. In this prospect, EDOT was first dissolved in distilled water, and then V$_2$O$_5$ was added to the solution under vigorous stirring. After repeated filtering and washing processes, the resulting bluish-black powder was dried in air.

The chemical compositions of the PEDOT/V$_2$O$_5$ hybrid samples we have currently synthesized were estimated from inductively coupled plasma optical emission spectroscopy (ICP-OES), CHNS and thermal analysis [16]. They are symbolized as VP1–VP5 (Tab. I). Let us recall that, to our knowledge, this is the first conducting polymer/V$_2$O$_5$ hybrid system synthesized starting with well-crystalline vanadium oxide.

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The incorporation of the polymer into the V$_2$O$_5$ was investigated using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). For the sake of clarity, the main remarkable results will be given here.

TABLE I Nominal EDOT/V$_2$O$_5$ Ratio and Corresponding Chemical Composition for the Hybrid Samples.

	Nominal EDOT/V$_2$O$_5$	Chemical composition*
VP1	0.02	$(C_6H_4O_2S)_{0.02}V_2O_{4.9}$
VP2	0.04	$(C_6H_4O_2S)_{0.03}V_2O_{4.8}$
VP3	0.08	$(C_6H_4O_2S)_{0.05}V_2O_{4.7}$
VP4	0.40	$(C_6H_4O_2S)_{0.18}V_2O_{4.6}$
VP5	0.60	$(C_6H_4O_2S)_{0.25}V_2O_{4.6}$

*The surface-adsorbed water contents are ignored.

4.1 Fourier Transform Infrared Spectroscopy

If it does occur, the intercalative redox polymerization of PEDOT, which is a p-type conductor, into V_2O_5 must lead to the reduction of vanadium ions, leading to significant changes in the vibration peaks of the vanadium oxide framework [16]. The spectra of the hybrids shown in Figure 2 display the characteristic bands corresponding to both PEDOT and V_2O_5. Vibrations around 1520, 1450, and 1380 cm^{-1} are assigned to the stretching of C=C and C–C in the thiophene ring, and those at 1130 and 1090 cm^{-1} to the stretching of the ethylenedioxy group [22–28]. These peaks increase as the amount of incorporated polymer augments, which proves the presence of the PEDOT in these materials. The absence of peaks at 1490 and 1190 cm^{-1} implies that the organics are not in monomer form but in polymeric form, thereby confirming polymerization of EDOT. Moreover, the peaks around 1260 and 1090 cm^{-1} indicate that the polymer is in the expected p-doped state [23, 28]. Bands around 500 and 800 cm^{-1} are attributed to V–O–V stretching modes and those around 1000 cm^{-1} to V=O stretching. The significant changes of V=O peaks from VP1 to VP5 (Fig. 2(b)) would suggest a strong interaction (*e.g.*, hydrogen bonding) between the vanadyl group and the incorporated polymer, as it occurs for PPY/V_2O_5 xerogel hybrid [8], and also accounts for a greater number of V^{4+} centers in the hybrids. Related to the later point, recent EPR investigations on our hybrid samples, carried out at the Institute of General and Inorganic Chemistry (Bulgarian Academy of Sciences, 113 Sofia, Bulgaria), showed that the EDOT insertion into V_2O_5 originates an EPR signal from $[V^{4+}O^{2-}]^{2+}$, which increases with the amount of the incorporated polymer [29].

The mechanism of this remarkable all-solid-state intra-lamellar polymerization is presumed to be coupled to the ability of vanadium centers to activate the oxygens of the V=O groups, which are the primary electron acceptors in this process. In this way, vanadium
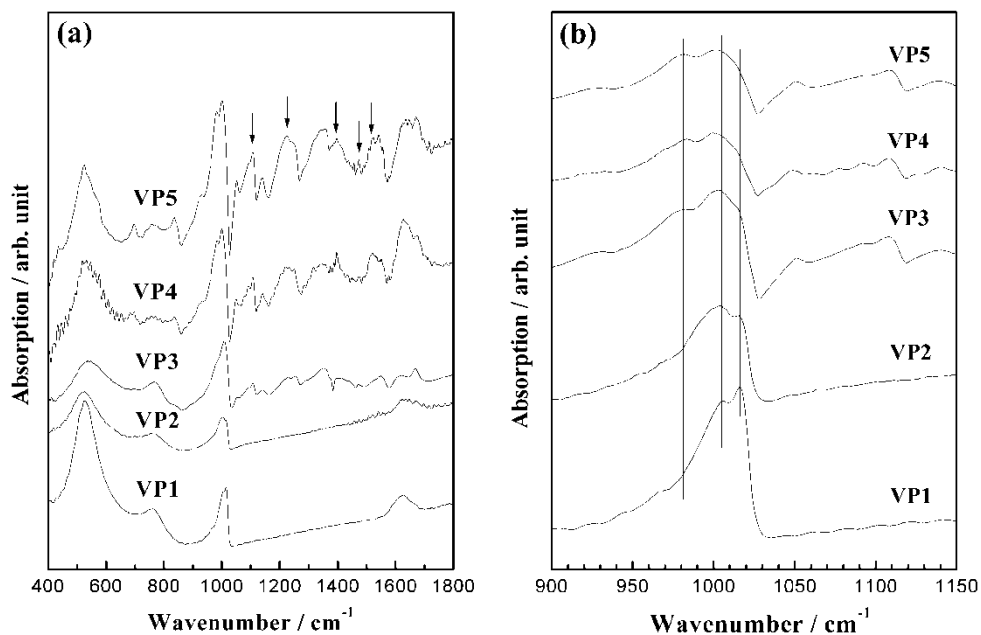

FIGURE 2   Infrared spectra for VP1–VP5, in the range of (a) 400~1800 cm^{-1} and (b) 900~1150 cm^{-1} (enlargement). The samples were diluted with KBr and pressed into a pellet. Some important peaks from polymer are marked with arrows.

oxide would play a direct role in the redox event, which is consistent with the ability of vanadium oxide to catalyze several oxidation reactions of organic molecules [30].

4.2 X-ray Diffraction Study

Figure 3 shows a series of well-developed $(0\,0\,l)$ peaks; they indicate that the d spacing increases from 4.3 to 13.8 Å and further to 19.0 Å depending on the amount of the incorporated macromolecules [21]. This would indicate that the expansion proceeds in two steps, first forming a monolayer of polymer and then double layers. However some $(h\,k\,0)$ reflections of the hybrids such as $(1\,1\,0)$ and $(3\,1\,0)$, which obviously correspond to those of the pristine V_2O_5, show a diffuse peak shape, rising rather rapidly and then declining slowly toward the high angle side. This feature suggests that the compounds have a random layer stacking structure, which consists of equidistant and parallel $(a–b)$ layers, but randomly rotated about the normal c-axis [25]. Let us quote that in the field of lithium battery such a feature is likely to favor the power density and the cycling life of corresponding electrode materials, according to our 'electrochemical model' quoted in Ref. [31].

4.3 Transmission Electron Microscopy

Additional evidence of PEDOT intercalation within the inter-lamellar space of V_2O_5 is illustrated in Figure 4 showing TEM micrographs: the pristine V_2O_5 consists of thick agglomerated particles with irregular sizes of micrometer order (Fig. 4(a)), whereas the particles of hybrids are composed of well-developed $(a–b)$ planes stacked along with the c-axis (Figs 4(b)–(d)). The stacking length in the c-direction is much shorter compared with a and b directions for the hybrids, which should be considered as the enhancement
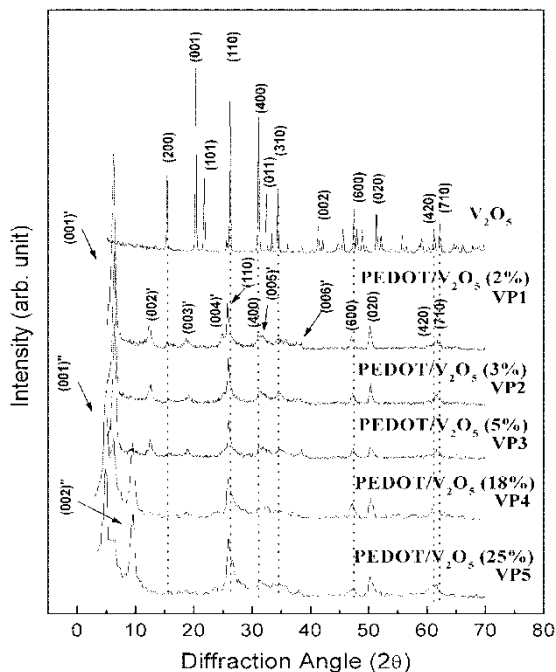

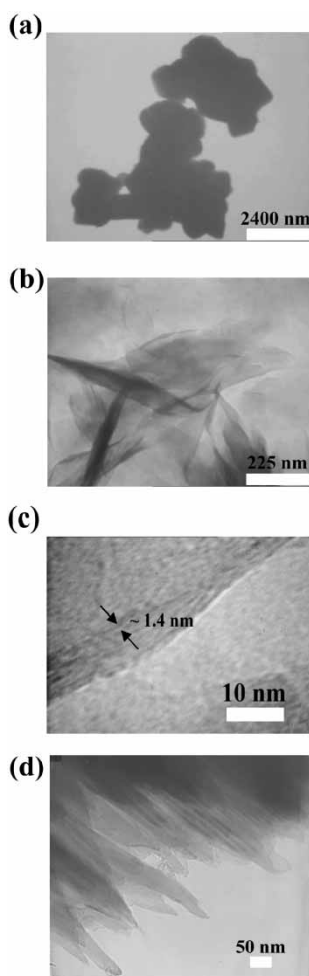FIGURE 3 Powder XRD patterns of pristine V_2O_5, VP1–VP5.

FIGURE 4   Transmission electron micrographs for (a) pristine V_2O_5, (b) and (c) VP1, and (d) VP5 [21].

of 'bidimensionality'. The interlayer spacing of VP1 has been estimated by measuring the length from one dark line to the nearest one, which gives $\sim$14 Å in good agreement with the XRD result.

5   ACHIEVEMENT OF V_2O_5/POLY(3,4-ETHYLENEDIOXYTHIOPHENE) HYBRIDS WITH A HIGH ELECTRICAL CONDUCTIVITY

Electrical conductivity was measured on pelletized samples ($10 \, ton \, cm^{-2}$) by a conventional four-probe method using conducting silver paint for contacts [16]. The electrical transport behaviors of the hybrids could be understood by considering the insertion of PEDOT into V_2O_5 powder as a hybrid system where two different types of p and n-type low-dimensional electronic conductors coexist at the molecular level in a dimensionally constrained environment. Two types of charge carriers should be present in these materials, that is, small polarons (electrons) associated with the d^1 (V^{4+}) centers in the vanadium oxide lattice, and large polarons (holes) in the PEDOT backbone. The actual nature of charge transport would

TABLE II Room-Temperature Electrical Conductivity for the Pristine V_2O_5 and Hybrids.

Sample	Conductivity ($S\,cm^{-1}$)
V_2O_5	8.78×10^{-5}
VP1	2.92×10^{-3}
VP2	6.97×10^{-3}
VP3	3.84×10^{-2}
VP4	9.82×10^{-2}
VP5	1.01×10^{-1}

depend on the relative mobility of these two different kinds of carriers. Therefore, the exact conduction mechanism may be complex. Let us simply quote here that the overall electronic conductivity of PEDOT/V_2O_5 hybrids is several orders of magnitude higher than that of pristine V_2O_5; it raises from 10^{-5} to $10^{-1}\,S\,cm^{-1}$ as the amount of incorporated polymer augments from VP1 to VP5 (Tab. II). The increase in conductivity is probably due to a continued process of growth of the organic polymer network. The conductivity was found to increase with rising temperature as has already been observed in most intercalated compounds and conjugated polymers [15, 32].

Acknowledgements

References

[1] Sanchez, C., Soler-Illia, G. J. de A. A., Ribot, F., Lalot, T., Mayer, C. R. and Cabuil, V. (2001). *Chem. Mater.*, **13**, 3061–3083.
[2] Portier, J., Campet, G., Treuil, N., Poquet, A., Kim, Y. I., Kwon, S. J., Kwak, S. Y. and Choy, J. H. (1998). *J. Korean Chem. Soc.*, **42**, 487–500.
[3] Gangopadhyay, R. and De, A. (2000). *Chem. Mater.*, **12**, 608–622.
[4] Colvin, V. L., Schlamp, M. C. and Alivisatos, A. P. (1994). *Nature (London)*, **370**, 354.
[5] Leroux, F., Koene, B. E. and Nazar, L. F. (1996). *J. Electrochem. Soc.*, **143**, L181.
[6] Leroux, F., Goward, G., Power, W. P. and Nazar, L. F. (1997). *J. Electrochem. Soc.*, **144**, 3886.
[7] Goward, G. R., Leroux, F. and Nazar, L. F. (1998). *Electrochim. Acta*, **43**, 1307.
[8] Wong, H. P., Dave, B. C., Leroux, F., Harreld, J., Dunn, B. and Nazar, L. F. (1998). *J. Mater. Chem.*, **8**, 1019.
[9] Harreld, J. H., Dunn, B. and Nazar, L. F. (1999). *Int. J. Inorg. Mater.*, **1**, 135.
[10] Lira-Cantu, M. and Gomez-Romero, P. (1999). *Int. J. Inorg. Mater.*, **1**, 111.
[11] Lira-Cantu, M. and Gomez-Romero, P. (1999). *J. Electrochem. Soc.*, **146**, 2029.
[12] Lira-Cantu, M. and Gomez-Romero, P. (1999). *J. Solid State Chem.*, **147**, 601.
[13] Kanatzidis, M. G. and Wu, C. G. (1989). *J. Am. Chem. Soc.*, **111**, 4141.
[14] Liu, Y. J., DeGroot, D. C., Schindler, J. L., Kannewurf, C. R. and Kanatzidis, M. G. (1993). *J. Chem. Soc. Chem. Commun.*, 593.
[15] Wu, C. G., Degroot, D. C., Marcy, H. O., Schindler, J. L., Kannewurf, C. R., Liu, Y. J., Hirpo, W. and Kanatzidis, M. G. (1996). *Chem. Mater.*, **8**, 1992.
[16] Kwon, C. W. (2002). *PhD thesis*, Bordeaux I University, France.
[17] For general reviews on conductive polymers, see: Nalwa, H. S. (Ed.) (1997). *Handbook of Organic Conductive Molecules and Polymers*, Vols. 1–4, Wiley, Chichester, UK.
[18] Groenedaal, L. B., Jonas, F., Freitag, F., Pielartzik, H. and Reynolds, J. R. (2000). *Adv. Mater.*, **12**, 481.
[19] Murugan, A. V., Kale, B. B., Kwon, C. W., Campet, G. and Vijayamohanan, K. (2001). *J. Mater. Chem.*, **11**, 2470.
[20] Murugan, A. V., Kwon, C. W., Campet, G., Kale, B. B., Maddanimath, T. and Vijayamohanan, K. (2002). *J. Power Sources*, **105**, 1.
[21] Kwon, C. W., Murugan, A. V., Campet, G., Portier, J., Kale, B. B., Vijaymohanan, K. and Choy, J. H. (2002). *Electrochem. Commun.*, **4**, 384.
[22] Gustafsson, J. C., Liedberg, B. and Inganas, O. (1994). *Solid State Ionics*, **69**, 145.

[23] Kvarnstrom, C., Neugebauer, J., Blomquist, S., Ahonen, H. J., Kankare, J. and Ivaska, A. (1999). *Electrochem. Acta*, **44**, 2739.
[24] Hernandez, V., Ramirez, F. J., Otero, T. F. and Lopez Navarrete, J. T. (1994). *J. Chem. Phys.*, **100**, 114.
[25] Aasmundtveit, K. E., Samuelson, E. J., Pettersson, L. A. A., Inganas, O., Johansson, T. and Feidenhans'l, R. (1999). *Synth. Met.*, **101**, 561.
[26] Aasmundtveit, K. E., Samuelson, E. J., Inganas, O., Pettersson, L. A. A., Johansson, T. and Ferrer, S. (2000). *Synth. Met.*, **113**, 93.
[27] Zotti, G., Zecchin, S., Schiavon, G. and Groenendaal, L. B. (2000). *Chem. Mater.*, **12**, 2996.
[28] Tran-Van, F., Garreau, S., Louarn, G., Froyer, G. and Chevrot, C. (2001). *J. Mater. Chem.*, **11**, 1378.
[29] Stoyanova, R. and Zhecheva, E. [private communication].
[30] Ross, R. A. and Fairbridge, C. (1984). *Can. J. Chem.*, **62**, 1483.
[31] Treuil, N., Labrugère, C., Menetrier, M., Portier, J., Campet, G., Hwang, S. J. and Choy, J. H. (1999) *J. Phys. Chem. B*, **103**(12), 2100.
[32] Javadi, H. H., Cromack, K. R., McDiarmid, A. G. and Epstein, A. (1989) *Phys. Rev. B*, **39**, 3579.